

2

AD-A228 139

DTIC FILE COPY

COMPUTATIONAL ANALYSES OF STRUCTURAL
PROPERTIES OF THE DINITRAMIDE ION, $N(NO_2)_2^-$, AND
SOME RELATED MOLECULES: $HN(NO_2)_2$ AND $N(NO_2)_3$

Paul C. Redfern and Peter Politzer
Department of Chemistry
University of New Orleans
New Orleans, LA 70148



Accession For	
DTIC GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

Technical report submitted to the Office of Naval Research under contract no. N00014-85-K-0217

September 1990

DTIC
ELECTE
OCT 10 1990
S E D

DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

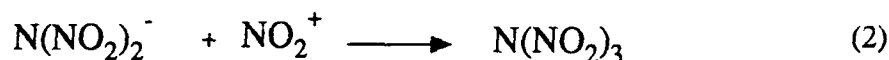
1a. REPORT SECURITY CLASSIFICATION unclassified			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release. Unlimited distribution.		
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE					
4. PERFORMING ORGANIZATION REPORT NUMBER(S)			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION University of New Orleans Department of Chemistry		6b. OFFICE SYMBOL (If applicable)		7a. NAME OF MONITORING ORGANIZATION Office of Naval Research Code 1132P	
6c. ADDRESS (City, State, and ZIP Code) University of New Orleans Department of Chemistry New Orleans, LA 70148				7b. ADDRESS (City, State, and ZIP Code) Office of Naval Research Code 1132P Arlington, VA 22217	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research		8b. OFFICE SYMBOL (If applicable)		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-85 K-0217	
8c. ADDRESS (City, State, and ZIP Code) Office of Naval Research Code 1132P Arlington, VA 22217		10. SOURCE OF FUNDING NUMBERS			
		PROGRAM ELEMENT NO.		PROJECT NO.	TASK NO.
					WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) COMPUTATIONAL ANALYSES OF STRUCTURAL PROPERTIES OF THE DINITRAMIDE ION, $N(NO_2)_2^-$, AND SOME RELATED MOLECULES: $HN(NO_2)_2$ AND $N(NO_2)_3$					
12. PERSONAL AUTHOR(S) Paul C. Redfern and Peter Politzer					
13a. TYPE OF REPORT Technical report		13b. TIME COVERED FROM _____ TO _____		14. DATE OF REPORT (Year, Month, Day) 1990 September	
15. PAGE COUNT 7					
16. SUPPLEMENTARY NOTATION 2-1					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP			
19. ABSTRACT (Continue on reverse if necessary and identify by block number) We have carried out <u>ab initio</u> SCF calculations of the structures of the dinitramide anion, $N(NO_2)_2^-$, and some related molecules: $HN(NO_2)_2$ and $N(NO_2)_3$. We have analyzed factors affecting their stabilities, and computed the proton affinity of $N(NO_2)_2^-$ [as a measure of the acidity of $HN(NO_2)_2$] and the interaction energy of $N(NO_2)_2^-$ with NO_2^+ to yield $N(NO_2)_3$. The proton affinity of $N(NO_2)_2^-$ was found to be considerably greater than that of NO_2^- .					
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION unclassified		
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. Peter Politzer			22b. TELEPHONE (Include Area Code) (504) 286-6850		22c. OFFICE SYMBOL

Introduction

In response to the interest in the dinitramide anion, $\text{N}(\text{NO}_2)_2^-$, that has resulted from Schmitt and Bottaro's recent synthesis of several dinitramide salts,¹ we have carried out a computational analysis of its structure and some of its properties. Since there is also interest in the conjugate acid, $\text{HN}(\text{NO}_2)_2$ [the existence of which has not been established], we have included it in this study. This permits us to estimate the proton affinity of the dinitramide anion, which corresponds to ΔE for the process,



Finally, since we had earlier investigated the possible stability of the molecule $\text{N}(\text{NO}_2)_3$,² we also determined ΔE for the reaction,



The results of these studies are summarized in this report.

Methods

Our general approach involved *ab initio* SCF computations, using the GAUSSIAN 88 system of programs.³ Geometries were optimized with the MIDI1 basis set, which is obtained by splitting the most diffuse valence s and p functions on each atom;⁴ it is very nearly equivalent to the 3-21G basis, which is known to be generally reliable for computing structures, even for negative ions.⁵ For $\text{HN}(\text{NO}_2)_2$, however, we modified this procedure because both 3-21G and MIDI1 optimizations predicted planarity for this molecule, which we considered suspect because Ritchie has shown that 3-21G calculations erroneously yield a planar structure for the related system $\text{H}_2\text{N}-\text{NO}_2$.⁶ Accordingly we first determined all angles in $\text{HN}(\text{NO}_2)_2$ at the 6-31G* level (which had correctly predicted $\text{H}_2\text{N}-\text{NO}_2$ to be pyramidal⁶) and then carried out MIDI1 optimizations of the bond lengths. The final energies for all of the systems investigated were computed by single-point runs with the MIDI1p basis set, which is obtained by enlarging the MIDI1 through the addition of a diffuse p function to each first-row atom (e.g. N, O, etc.).

While these calculations are at the *ab initio* SCF level and hence do not take account of electron correlation, it is nevertheless anticipated that the ΔE values obtained for eqs. (1) and (2) will be meaningful, because their reactions involve only closed-shell systems and no electron pairs are disrupted. We tested this point on the nitrite ion, NO_2^- , and its conjugate acid, HNO_2 (HONO),

Table 1. Proton affinity of NO_2^- calculated at various *ab initio* SCF levels.

Basis set	3-21G	MIDI1	MIDI1p	combined ^a MIDI1p//MIDI1	6-31+G	exp ^b
Proton affinity (kcal/mole)	364	364	333	333	330	338

^aIn this instance, MIDI1 was used for geometry optimization and MIDI1p for computing energies.

This is the approach used to obtain the results that will be presented for $(\text{NO}_2)_2^-$.

^bS. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin and W. G. Mallard, J. Phys. Chem. Ref. Data 17, Suppl. No. 1, (1988).

using five different basis sets. All five correctly predicted that NO_2^- is protonated on an oxygen rather than on nitrogen, and all of them predicted the energy difference between the cis and trans forms of HONO to within 2.1 kcal/mole of the experimentally-determined value. Finally, Table 1 presents the proton affinities computed for NO_2^- ; these have been corrected for the difference in zero-point energies, using a semi-empirical (AM1) estimate of 7.3 kcal/mole.

Table 1 shows that both the MIDI1p basis set and the combined MIDI1p//MIDI1 yield very good NO_2^- proton affinities. The latter is the approach that was used for $\text{N}(\text{NO}_2)_2^-$ in this work, because we found it to produce better geometries than does the MIDI1p.

Results

Our calculated energies and structures for $\text{N}(\text{NO}_2)_2^-$, $\text{HN}(\text{NO}_2)_2$, NO_2^+ and $\text{N}(\text{NO}_2)_3$ are given in Table 2. The protonation of $\text{N}(\text{NO}_2)_2^-$ to give $\text{HN}(\text{NO}_2)_2$ could, in principle, occur on the central nitrogen or any of the four oxygens. We tested all of these possibilities and found that the site most favored energetically is the nitrogen, although the oxygen protonations are only 4 to 8 kcal/mole less stable.

Gilardi has carried out crystallographic determinations of the structures of a series of dinitramide salts synthesized by Schmitt and Bottaro. The ranges of bond lengths and bond angles obtained for two of these, ammonium dinitramide (I) and the 1,2,4,7-tetrammonio salt of cubane (II), are summarized in Table 3.

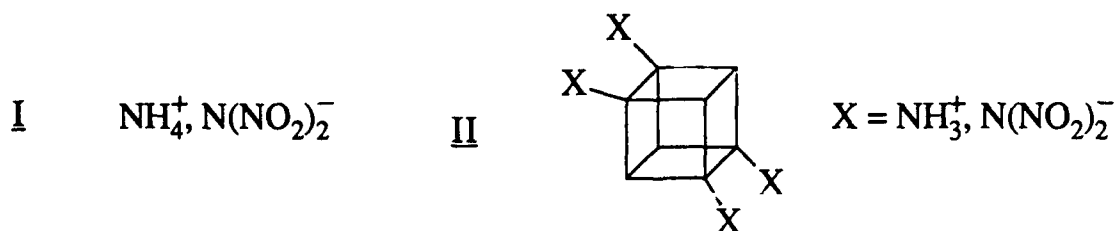


Table 2. Calculated *ab initio* SCF energies (MIDI1p) and structures (MIDI1).

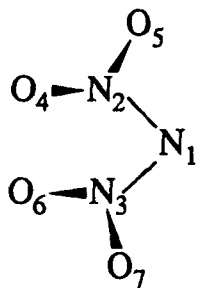
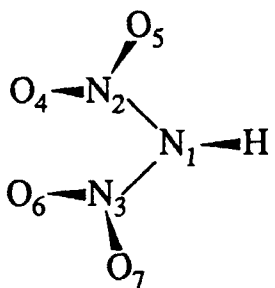
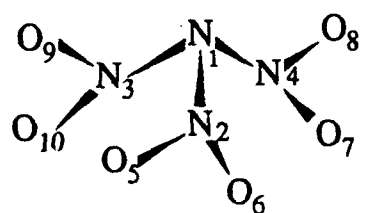
Molecule and Energy, hartrees		Distance, Å	Angle, deg.
N(NO ₂) ₂ ⁻ : C ₂ symmetry E = -459.7946		N-N: 1.410	N-N-N: 110
		N ₂ -O ₄ , N ₃ -O ₆ : 1.254 N ₂ -O ₅ , N ₃ -O ₇ : 1.258	N ₁ -N ₂ -O ₄ } 124 N ₁ -N ₃ -O ₆ } N ₁ -N ₂ -O ₅ } 113 N ₁ -N ₃ -O ₇ } O-N-O: 123 O ₄ -N ₂ -N ₁ -N ₃ } -28 O ₆ -N ₃ -N ₁ -N ₂ }
HN(NO ₂) ₂ : C _s symmetry E = -460.2664		N-N: 1.433	N-N-N: 121
		N-H: 1.007 N ₂ -O ₄ , N ₃ -O ₆ : 1.221 N ₂ -O ₅ , N ₃ -O ₇ : 1.243	N ₂ -N ₁ -H } 110 N ₃ -N ₁ -H } N ₁ -N ₂ -O ₄ } 119 N ₁ -N ₃ -O ₆ } N ₁ -N ₂ -O ₅ } 112 N ₁ -N ₃ -O ₇ } O-N-O: 129 H ₄ -N ₁ -N ₂ -N ₃ : 110 O ₄ -N ₂ -N ₁ -N ₃ : -36 O ₆ -N ₃ -N ₁ -N ₂ : 36
NO ₂ ⁺ : linear, O-N-O E = -202.4039		N-O: 1.122	
N(NO ₂) ₃ : C ₃ symmetry; pyramidal E = -662.4265		N-N: 1.524	N-N-N: 107
		N ₂ -O ₅ , N ₃ -O ₇ , N ₄ -O ₉ : 1.213 N ₂ -O ₆ , N ₃ -O ₈ , N ₄ -O ₁₀ : 1.223	O-N-O: 133 N ₁ -N ₂ -O ₅ } 111 N ₁ -N ₃ -O ₇ } N ₁ -N ₄ -O ₉ } N ₁ -N ₂ -O ₆ } 116 N ₁ -N ₃ -O ₈ } N ₁ -N ₄ -O ₁₀ }

Table 3. Crystallographically-determined ranges of bond lengths and bond angles in $\text{N}(\text{NO}_2)_2^-$ ions of I and II.

Bond length, Å	Bond angle, deg.
N-N: 1.356 - 1.390	N-N-N: 113.2 - 115.9
N-O _a : 1.227 - 1.251	N-N-O _a : 110.9 - 113.0
N-O _b : 1.210 - 1.228	N-N-O _b : 123.4 - 127.0
	O-N-O: 121.3 - 123.3

^aThe crystallographic data were kindly provided by Dr. Richard Gilardi.

A comparison of Tables 2 and 3 shows that there is generally good agreement between the calculated and experimental structures of $\text{N}(\text{NO}_2)_2^-$, particularly in view of the fact that the latter are for the ion in crystalline environments, subject to packing effects, while the former corresponds to the gaseous phase. In particular, the computed structure reproduces the observed difference of approximately 10° between the two N-N-O angles of each nitro group. This can probably be attributed to steric interference between O₄ and O₆ (Table 2), and the consequent tendencies of these two oxygens to move away from each other; their separation is 2.61 Å, significantly less than the sum of their van der Waals radii, 3.0 Å.⁷ Thus the steric factor remains important.

As a point of interest, we also computed the energy of the non-equilibrium form of the dinitramide ion in which the N-N-N angle is forced to be 180° . In this situation, the NO_2 groups are observed to rotate so as to be in perpendicular planes. This $\text{N}(\text{NO}_2)_2^-$ structure was found to be 51 kcal/mole less stable than the equilibrium form shown in Table 2.

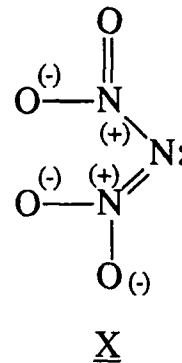
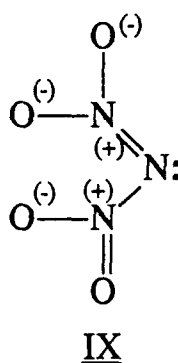
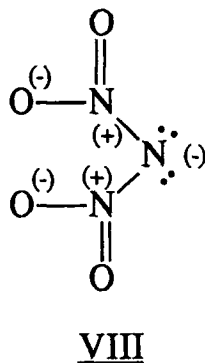
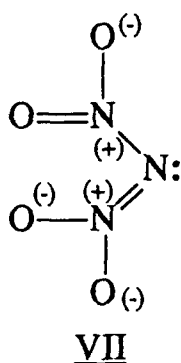
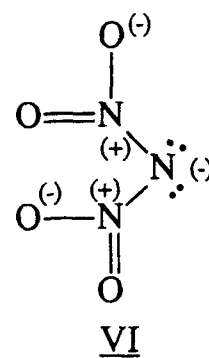
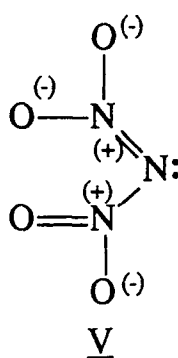
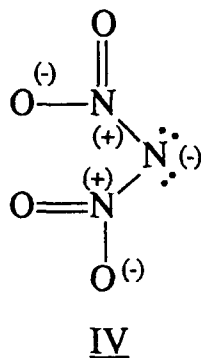
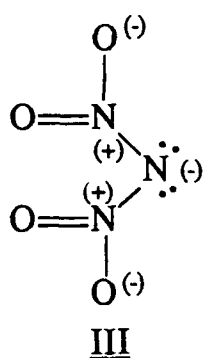
Both $\text{HN}(\text{NO}_2)_2$ and $\text{N}(\text{NO}_2)_3$ show differences between the two N-N-O angles within each nitro group, but they are smaller than in $\text{N}(\text{NO}_2)_2^-$, 7° and 5° respectively. Presumably steric factors are again responsible; the relevant O...O separations in the two molecules are 2.69 Å and 2.78 Å.

The proton affinity of $\text{N}(\text{NO}_2)_2^-$ is predicted to be 289 kcal/mole, based again upon an AM1 estimate of the difference in zero-point energies (7.2 kcal/mole). This indicates that the gaseous phase acidity of $\text{HN}(\text{NO}_2)_2$ is greater than that of HNO_2 . Finally, ΔE for reaction (2) is found to be -143 kcal/mole (uncorrected for zero-point energy differences).

Discussion

The dinitramide ion, $\text{N}(\text{NO}_2)_2^-$, can be described in terms of the resonance structures III-X. Their contributions are far from equal however. The formal charges suggest that VIII - X are rather unlikely, due to proximities of strongly negative oxygens, whereas III should be favored. These expectations are confirmed by the calculated structures (the $\text{N}_2\text{-O}_4$ and $\text{N}_3\text{-O}_6$ bonds are

shorter than the $\text{N}_2\text{-O}_5$ and $\text{N}_3\text{-O}_7$) and especially by the crystallographic results (the N-O_b bonds are shorter than the N-O_a).



Our calculations show the two nitro groups in $\text{N}(\text{NO}_2)_2$ to be rotated out of the N-N-N plane by 28° . This may in part represent a further effort by O_4 and O_6 to increase their separation; however we believe that it also reflects some delocalization of the two lone pairs on the central nitrogen, leading to contributions from V and VII. Assuming that the electron pairs around the central nitrogen are distributed tetrahedrally (which is supported by the N-N-N angle of 110°), then a 28° rotation of the NO_2 planes makes them essentially perpendicular (dihedral angles = 92°) to the lone pair orbitals, thereby optimizing conjugation. This reasoning provides an explanation for the fact that in $\text{HN}(\text{NO}_2)_2$ the nitro groups are rotated by 36° in *opposite* directions, rather than in the same direction as in $\text{N}(\text{NO}_2)_2$; in $\text{HN}(\text{NO}_2)_2$ there is only one lone pair available for conjugation, and opposite rotations allow both nitro groups to interact with it.

Somewhat surprisingly, we found that when the NO_2 groups in $\text{N}(\text{NO}_2)_2$ are forced to be in the N-N-N plane, the molecular energy increases by only 1.1 kcal/mole, suggesting that the conjugation has been only slightly impaired. Even when one of the groups is subsequently made to rotate by 90° , so that it is perpendicular to the N-N-N plane, the energy goes up by only an additional 0.2 kcal/mole; evidently the other NO_2 is now able to conjugate with *both* lone pairs. Only when both NO_2 groups are forced to be perpendicular to the N-N-N plane is there significant

destabilization, by 21 kcal/mole relative to the ground state. Our finding that there is very little energy barrier to small rotations of the nitro groups in $\text{N}(\text{NO}_2)_2$ is consistent with Gilardi's observation that the degrees of NO_2 rotation vary from one dinitramide salt to another; for example they are roughly $20^\circ - 25^\circ$ in I but less than 10° in II.

Another aspect of the conjugation between the NO_2 groups and the lone pairs in $\text{N}(\text{NO}_2)_2$ is brought out by our observation that when the N-N-N angle is forced to be 180° , the nitro groups rotate so as to be in perpendicular planes. In this linear arrangement, the two lone pairs are expected to be in perpendicular p-type orbitals; thus, conjugation with the nitro groups can occur most effectively when these are also perpendicular. We have used analogous reasoning in the past to explain why the NO_2 substituents in dinitroacetylene are in perpendicular planes.⁸

It is interesting to observe the marked increase in the N-N bond length, about 0.1 \AA , in going from $\text{N}(\text{NO}_2)_2$ and $\text{HN}(\text{NO}_2)_2$ to $\text{N}(\text{NO}_2)_3$. This is probably at least partially due to the fact that three NO_2 groups are now competing to conjugate with the single lone pair on the central nitrogen; thus the degree of conjugatively-produced double bond character in each N-N bond is considerably reduced. The nitro groups in $\text{N}(\text{NO}_2)_3$ are rotated more (41°) than in either $\text{N}(\text{NO}_2)_2$ or $\text{HN}(\text{NO}_2)_2$. While our calculations do indicate that there is at least a local energy minimum corresponding to $\text{N}(\text{NO}_2)_3$, the lengths of the N-N bonds suggest that the molecule may be rather unstable. (For comparison, our calculated N-N distance in hydrazine, N_2H_4 , at essentially the same computational level, is 1.449 \AA , in exact agreement with the experimentally-determined value.⁹)

References

1. R. Schmitt and J. Bottaro, presented at energetic materials workshops, Naval Weapons Center, China Lake, CA, December 1989 and June 1990.
2. This was suggested to us by Professor George A. Olah.
3. GAUSSIAN 88: M. J. Frisch, M. Head-Gordon, H. B. Schlegel, K. Raghavachari, J. S. Binkley, C. Gonzalez, D. J. Defrees, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. Martin, L. R. Kahn, J. J. P. Stewart, E. M. Fluder, S. Topiol and J. A. Pople, GAUSSIAN 88, Gaussian Inc., Pittsburgh, PA, 1988.
4. S. Huzinaga, J. Andzelm, M. Klobukowski, E. Radzio-Andzelm, Y. Sakai and H. Tatewaki, Gaussian Basis Sets for Molecular Calculations, Elsevier, Amsterdam, 1984.
5. W. J. Hehre, L. Radom, P. v. R. Schleyer and J. A. Pople, Ab Initio Molecular Orbital Theory, John Wiley and Sons, New York, 1986.
6. J. P. Ritchie, J. Am. Chem. Soc. 107, 1829 (1985); 111, 2517 (1989).
7. A. Bondi, J. Phys. Chem. 68, 441 (1964).
8. P. Politzer and R. Bar-Adon, J. Am. Chem. Soc. 109, 3529 (1987).
9. J. S. Murray, N. Sukumar, S. Ranganathan and P. Politzer, Int. J. Quantum Chem. 37 611 (1990).